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<p>(54) Title: CLEANING PROCESS</p> <p>(57) Abstract</p> <p>The invention relates to a process for cleaning substrate with acoustic energy by using degassed wash liquor. Degassed wash liquor can for example be achieved by adding gas whereafter a gas-to-no-gas system is activated.</p>	

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Cleaning Process

Technical Field

- 5 The present invention relates to a process for cleaning substrate, especially fabrics, with acoustic energy and to detergent compositions suitable for use in such a process.

Prior Art & Background

- 10 Processes for cleaning substrate with acoustic energy are known in the art. Such processes using ultrasonic waves have for example been described in DE 36 31 727, DE 36 31 318, DE 36 30 183, DE 36 11 422 and DE 36 10 386.
- 15 When acoustic energy is applied to substrate in the liquid medium, it is believed that the sequence of pressure minima and maxima results in the formation and subsequent collapse of cavities that are accompanied by violent turbulences and vibrations. When soiled objects are immersed in a wash
- 20 liquor are subjected to acoustic energy, the soil will participate in this movement and will be removed from the object, due to cavitation forces. Ultrasonic waves are one form of acoustic energy.
- 25 Washing machines that make use of ultrasonic waves for cleaning purposes are known in the art. Examples are described in EP-A-0,261,363, EP-A-288378, DD 255756 and GB-A-2181041.
- 30 Costs of the acoustic energy equipment and the energy consumption of the acoustic transducers often are not in balance with the achieved improvement in cleaning performance of the acoustic washing process. This may be the main reason why acoustic energy techniques are not
- 35 widely used for cleaning processes.

Various techniques to improve acoustic energy cleaning processes have been proposed, amongst others techniques involving gasses. Two approaches relating to gas bubbles in the wash liquor can be distinguished in the prior art, both
5 claiming to improve the wash results.

The first approach in the art is to increase the amount of gas bubbles in the wash liquor when applying acoustic energy by supplying gas to the wash liquor as e.g.
10 described in JP 62189089, BE 903487 and in JP 60242881. However, this approach requires high energy input whereas it does not result in good washing performances.

The second prior art approach is to minimise the effect of
15 air bubbles on the cleaning process in acoustic energy cleaning.

EP-A-0,258,816 (JP 63066372) describes several ways to suppress the level of micro dispersed rest air bubbles
20 present in the wash liquor during ultrasonic washing processes, especially air present on fabric fibres and in the pores of fibres. This can be achieved by slowly agitating the wash load, pre-wetting the objects to be cleaned, using surfactants with good wetting properties,
25 applying ultrasonics for short periods with pauses in between and applying ultrasonics with alternating frequencies. However, this approach has amongst others the disadvantage that the washing machine needs to be equipped with an agitator and with special generators and
30 transducers for producing alternating frequencies. Further, formulation flexibility of the detergent is diminished, as only specific surfactants can be used. Furthermore, total washing time will increase due to pre-wetting and to pausing between application of ultrasonics. Moreover, this
35 ultrasonic wash process results in stain spotting on substrate which is thought to be caused by micro dispersed rest air bubbles.

US-A-4,907,611 describes deaerating wash liquor by using a boiling vessel whereafter it can be used for ultrasonic washing. This method not only has the disadvantage that investments are needed in the equipment, but also that much
5 energy is needed to raise the temperature of the wash liquor to the boiling temperature.

DE-B-1,194,225 describes partial deaeration of the wash liquor before applying ultrasonic. Deaeration can be
10 achieved by filtering the wash liquor or by using vacuum pumps. These methods however have the disadvantage that high investments are needed in the equipment, i.e. filter installations and/or vacuum pumps. Further, the equipment can be dangerous and requires a lot of energy to be
15 effective when used, i.e. pressure for the filtering installations and low pressure for the vacuum pumps.

It is known from NL 6403654 (US-A-3,402,075) that application of ultrasonic energy to water creates a
20 dispersion of air bubbles, disturbing the distribution of ultrasonic waves through the wash liquor. This results in less effective washing effects of the ultrasonic waves. The document suggests to use certain surfactants to improve removal of air bubbles from the wash liquor. However,
25 neither removing the air bubbles that are created after applying ultrasonic energy nor using the specific surfactants will lead to acceptable washing results.

It is considered that the low effectiveness of washing
30 processes with acoustic energy, the high investment in the equipment and the high amount of energy used are the main prohibitive reasons why acoustic energy has only been used on a restricted scale such as for the cleaning of instruments and watches.

35

It is the main object of the present invention to improve the effectiveness of acoustic washing processes, especially

with respect to the formation of stain spots, whereas preferably the process is also improved by lower cost implications for equipment and energy use.

- 5 Surprisingly, it has now been found that improved washing performances can be achieved if the amount of gas present in the wash liquor during the application of acoustic energy is kept low, preferably if the wash liquor is degassed.

10

Definition of the invention

According to the invention, there is provided a process for cleaning substrate in wash liquor with acoustic energy, characterised in that the wash liquor is degassed by using

- 15 a chemical reaction.

A second aspect of the invention concerns a detergent composition suitable for use in acoustic energy washing processes comprising effervescent material and a release

- 20 controlled gas-to-non-gas converting system.

A third aspect of the invention provides the use of a detergent composition comprising effervescent material to achieve a degassed wash liquor.

25

Description of the invention

Without wishing to be bound by any theory, it is believed that in line with the shock waves caused by the cavitation phenomena, the molecules present in the wash load move

30 apart and together. Gas present in the wash liquor, in the form of bubbles and in dissolved form, is thought to participate in this movement leading to excessive and ineffective cavitation in the bulk of the wash liquor.

Further, the resonating gas may reduce the energy

- 35 transferred to the substrate because of reflection and scattering phenomena. Furthermore, gas cavitation near the surface of the substrate is thought to cause stain

spotting. It is believed that lowering the amount of gas present in the wash liquor leads to less energy absorption which contributes to more effective use of acoustic energy, improved washing results, less stain spotting and lower
5 energy costs.

Suggestions in the prior art for degassing wash liquor have focused on the removal of gas bubbles, e.g. attached to fabric, or to remove the gas bubbles that are created
10 through the application of ultrasonic energy. However, both approaches only lead to partially degassed wash liquor, as only gas bubbles are removed. There is still gas present in dissolved state during application of ultrasonic energy.

15 Preferably, the amount of gas present in the washing liquor during application of acoustic energy is less than 0.48 mmol/l, more preferably 0.47 mmol/l, most preferably 0.44 mmol/l or less and in particular preferred 0.40 mmol/l or less. Preferably, the amount of gas in the wash liquor is 0
20 mmol/l or higher. However as low levels of gas may be difficult to achieve, the amount of gas in the wash liquor is more preferably 0.05 mmol/l or higher, most preferably 0.10 mmol/l or higher, particularly 0.15 mmol/l or higher.

25 The amount of gas present in the wash liquor can be determined by methods known in the art. An example of indirect determination is the determination of the amount of oxygen in the wash liquor, e.g. with an oxygen electrode, such as an Mikroprozessor OXI-Meter OXI 96. The
30 total level of air can be calculated on the basis thereof, using Henry's law as described in "Transport Phenomena Data Companion", L.P.B.M. Janssen & M.M.C.G. Warmoeskerken, Delftse Uitgevers Maatschappij, 1987, page 136.

35 Examples of gasses are oxygen, nitrogen and carbondioxide, NH₃ and inert gasses.

Applicants have also found that gas from the environment only diffuses slowly into degassed wash liquor. This makes the processes according to the present invention particularly suitable when the amount of gas present in the wash liquor meets the above gas requirements before, during and/or after, preferably before and/or during the application of acoustic energy.

As pointed out above in the prior art discussion, the reduction of the amount of gas in the wash liquor in the prior art is achieved by way of boiling the wash liquor, using physical mechanical means or combinations thereof.

According to the present invention the wash liquor is deaerated by using chemical reactions. An example of a chemical reaction to achieve degassed wash liquor is the addition of gas to the wash liquor after which a gas-to-non-gas converting system is activated. The gas may be added as such, i.e. by bubbling the gas into the wash liquor, or the gas may be produced by effervescent material.

Preferably, the gas that is added to the wash liquor is carbondioxide.

It is thought that when the gas bubbles to the wash liquor surface at least part of the gasses present in the wash liquor in dissolved state and/or in the form of bubbles is driven out, e.g. by absorption in the bubbles created by the added gas. The resulting wash liquor will mainly contain the added gas, in dissolved form and in the form of bubbles. Other gasses will mainly be removed from the wash liquor.

If used, effervescent material preferably reacts to produce a gas when it is brought in contact with water. An example of effervescent, carbondioxide producing material is a

carbonate-acid combination. Most preferably the carbonate and acid material are physically separated, e.g. by a coating or by storing in different containers. Examples of carbonate compounds are carbonate and bicarbonate salts of alkaline earth metals. The acids can be selected from any organic or anorganic acid, with a pKa of lower than the pKa of carbonate (i.e. $pK_a \leq 6.36$), e.g. citric acid, formic acid and acid forms of anionic surfactants.

10 Preferably, surface active detergent material is present during the addition of gas to the wash liquor. The presence of surface active detergent material is thought to lead to smaller gas bubbles that will bubble less quickly to the wash liquor surface, i.e. have a lower rising velocity and hence a longer residence time, stay longer in the wash liquor and being beneficial for the removal of other gas from the wash liquor.

20 Preferably, acoustic energy is applied to the wash liquor during the addition of the gas to the wash liquor. It is thought that the acoustic energy stimulates gas, present in dissolved state, to form bubbles.

A gas-to-non-gas converting system can be used to convert the added gas into a form, which form does not negatively interfere with the acoustic energy cleaning process, i.e. a non-gas form, such as a liquid, ionic or solid form. Preferably, the gas-to-non-gas converting system is activated after the added gas has become effective, i.e. after say e.g. 25% or more, preferably 30% or more, more preferably 40% or more and most preferably 45% or more of the gas, that was initially present in the wash liquor, has been removed from the wash liquor.

35 The choice of the gas-to-non-gas converting system will depend on the kind of gas added to the wash liquor. An example of a gas-to-non-gas converting system for

carbondioxide is a pH increasing system. It is thought that due to the pH increase, carbondioxide in the wash liquor will be transformed to carbonate ions. The pH increase system can be selected from any organic or in rganic
5 alkaline material, with a pKa that is higher than the pKa of carbonate, i.e. $pK_a \geq 6.36$, such as NaOH, KOH and Na-silicate.

Chemical removal of gas according to the above principle
10 may be effected by using specifically adapted detergent compositions, by using a washing machine with an automatic dosing system that sequentially doses ingredients according to a programme, by adding effervescent material and gas-to-non-gas converting system by hand or by combinations
15 thereof. Preferably, specifically adapted detergent compositions and/or sequentially dosing washing machines are used.

If automatic dosing systems for washing machines are used,
20 the effervescent material can be stored and dosed separately from the gas-to-non-gas converting system. Automatic dosing systems for washing machines are known in the art and for example described in GB 1,569,697. An example of a domestic automatic dosing system is the
25 Siwamat® plus electronic WE 49701 (ex Siemens).

If a detergent composition is used for achieving low amounts of gas in the wash liquor, the composition may comprise effervescent material and/or a gas-to-non-gas
30 converting system, preferably both. The gas-to-non-gas converting system and optionally the effervescent material may be release controlled. Examples of release controls are time, pH or temperature release controls, such as sachets and coatings.

35

There are no further restrictions to the other ingredients of the detergent compositions according to the present

invention, i.e. conventional ingredients can optionally be present such as surface active agents, builders, enzymes, fluoresces, perfumes, etc.

- 5 The surface active agents may be chosen from the surfactants described in "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by
- 10 Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. The surfactants preferably comprise one or more nonionic and/or anionic surfactants. They may also comprise amphoteric or zwitterionic detergent compounds,
- 15 but this is not normally desired owing to their relatively high cost.

- Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds
- 20 having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C₆-C₂₂ alkyl phenoethylene oxide
- 25 condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products of aliphatic C₈-C₁₈ primary or secondary linear or branched alcohols with ethylene oxide, generally 3 to 10 EO. Other examples of suitable nonionic surfactants are
- 30 alkylpolyglycosides and polyhydroxy fatty acid amide surfactants such as disclosed in WO-A-92/06154 (Procter & Gamble).

- Suitable anionic detergent compounds which may be used are
- 35 usually water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being

used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈-C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C₉-C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀-C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The preferred anionic detergent compounds are sodium C₁₂-C₁₈ alkyl sulphates.

Further, detergency builder may be used in detergent compositions according to the present invention in amounts of from 5 to 60%, preferably from 20 to 50% by weight. This detergency builder may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as an alkaline pH, the suspension of soil removed from the fabric and the suspension of the fabric-softening clay material.

Examples of suitable detergency builders include precipitating builders such as the alkali metal carbonates, bicarbonates, orthophosphates, sequestering builders such as the alkali metal tripolyphosphates or nitrilotriacetates, or ion exchange builders such as the amorphous alkali metal aluminosilicates or the zeolites.

Detergent compositions of the present invention may be provided in any form, for example as powders, aqueous liquids, non-aqueous liquids as well as gels or pastes. The latter may also be aqueous or non-aqueous.

Washing process

In the process of the present invention, soiled articles such as fabrics are immersed in an aqueous medium and radiated with acoustic energy, preferably ultrasonic energy. The principles of ultrasonic washing are well known in the art and can, for instance, be derived from the earlier mentioned EP-A-258 816 (Henkel). For the purpose of this application we define ultrasonic energy as usually involving frequencies of about 10 kilo Hertz (kHz) to about 100 kHz, however, higher frequencies of up to 10 mega Hertz (MHz) may also be used. In general, acoustic energy will be applied to the wash liquor in the wash phase for about 15 minutes or less, preferably between 0.25 to 10 minutes and more preferably between 0.5 to 5 minutes. As indicated above, acoustic energy can also be applied during the process of reduction of the amount of gas in the wash liquor, e.g. to stimulate dissolved gas to form bubbles.

Optionally, the wash load may be agitated slowly, preferably during "pulsing periods", i.e. periods in which no acoustic energy is applied to the wash load.

It should be pointed out here that the cleaning process of the present invention is not only suitable for cleaning fabrics, but the principle of the invention can also be applied in the cleaning of other soiled objects such as dishes and/or other table ware, or medical equipment.

The invention will now be further and non-limitatively illustrated in the following Examples.

EXAMPLE 1

Table 1 shows the amount of air that is saturated in water at several temperatures. These values can be calculated using Henry's law. Gas constants are for example given in
5 "Transport Phenomena Data Companion", L.P.B.M. Janssen & M.M.C.G. Warmoeskerken, Delftse Uitgevers Maatschappij, 1987, page 136.

TABLE 1

10	Temp. in °C	level of air in water in mmol/l
15	20	0.824
	30	0.710
	40	0.629
	50	0.578
	60	0.544

20

EXAMPLE 2

The amount of air in the experiments of NL 6403654 was determined applying ultrasonics with a power of 40W/l for
25 10 minutes to the wash liquor that comprised 0.025g/l Na-Dodecyl Benzene Sulphonate. The amount of air in the wash liquor was 0.48 mmol/l.

30 EXAMPLE 3

EMPA 101 test cloths of 7x7 cm (ex Eidgenössische material Prüfungsanstalt St. Gallen, Switzerland) were washed in a standard ELMA Ultrasonic bath comprising 8 liters of water of pH 9.5 comprising 1.75 g/l Na-Dodecyl Benzene Sulphonate
35 and 3.5 g/l STP, for 10 minutes at a temperature of 30°C with tap water comprising several air levels and were slightly moved with a mechanical stirrer.

The amount of gas present in the deaerated water was
40 calculated by determining the amount of oxygen using an

Mikroprozessor OXI Meter OXI 96. Based thereon and using Henry's Law, the amounts of N_2 , O_2 and CO_2 were calculated. δ Reflectance at 460 nm was determined. The results are presented in figure 1.

5

Figure 1 shows the δR (in %) on the Y-axis and the air level on the X-axis (in mmol/l).

It is clearly illustrated that wash results significantly improve when less air is present in the wash liquor.

10

EXAMPLE 4

The following wash experiments were performed in a standard ELMA Ultrasonex (US) bath containing 8 liters of water. US energy was varied and the operation frequency was 33 kHz.

15

EMPA 101 test cloths of 7x7 cm (ex Eidgenössische material Prüfungsanstalt St. Gallen, Switzerland) were washed for 10 minutes at a temperature of 30°C with normal tap water and with deaerated tap water. The fabrics were moved slightly with a mechanical stirrer. δ Reflectance at 460 nm was measured.

20

Deaerated water was prepared as follows:

25 Citric acid (conc. of 3 g/l) and Na-Dodecyl Benzene Sulphonate (conc. 1 g/l) were dissolved in water. Na-Bicarbonate (concentration of 3.6 g/l) was dissolved during application of ultrasonic energy. Small Carbondioxide bubbles were formed during 3-5 minutes. The pH was 5.5.

30 NaOH (conc. of 1.8 g/l) was added to pH 9.5.

30

The amount of gas present in the deaerated water was calculated by determining the amount of oxygen using an Mikroprozessor OXI Meter OXI 96. Based thereon and using Henry's Law, the amounts of N_2 , O_2 and CO_2 were calculated. The total amount of gas present in the deaerated water was 0.21 mmol/l.

35

Results are shown in table 2 with normal tap water and with deaerated water.

TABLE 2

5	US Energy Watt/l	δ Reflectance Normal tap water	δ Reflectance Deaerated water (0.21 gas mmol/l)
10	0 37.5	5 16	5 35

The table shows that wash results is significantly improved
15 in the deaerated wash liquor.

EXAMPLE 5

Experiments were carried out with ultrasonic radiation and deaeration of 8 liter wash liquor, similar to those
20 described in Example 4. In this case, however, the detergent and effervescent ingredients added were contained in two separate PVA (polyvinylalcohol) sachets.

Sachet 1 contained 8 g of Na-dodecylbenzene sulfonate, 24 g
25 of citric acid, and 29 g of Na-bicarbonate. Sachet 2 contained 42 g granular material, made up of 14% sodium hydroxide, 6.5% coconut fatty acid, 14% Zeolite 4A, 2% citric acid, and 4% bicarbonate.

30 One layer of PVA was used for sachet 1, and 4 layers were used for sachet 2. Both were added at the beginning of the wash.

The results of the experiment with ultrasonics and
35 degassing the wash liquor using sachets are illustrated in Figure 2.

Figure 2 shows the Air %, calculated on the basis of the O₂ level present (left Y-axis), the resulting pH, in pH units
40 (right Y-axis) and the time, in minutes (X-axis). The thick

line represents the pH and the thin line the % Air in time. The arrow indicates the start of the washing cycle.

The averages reflectance increase on EMPA 101 was 36 units, viz. practically identical to the ultrasonic wash results with deaeration of Table 2.

EXAMPLE 6

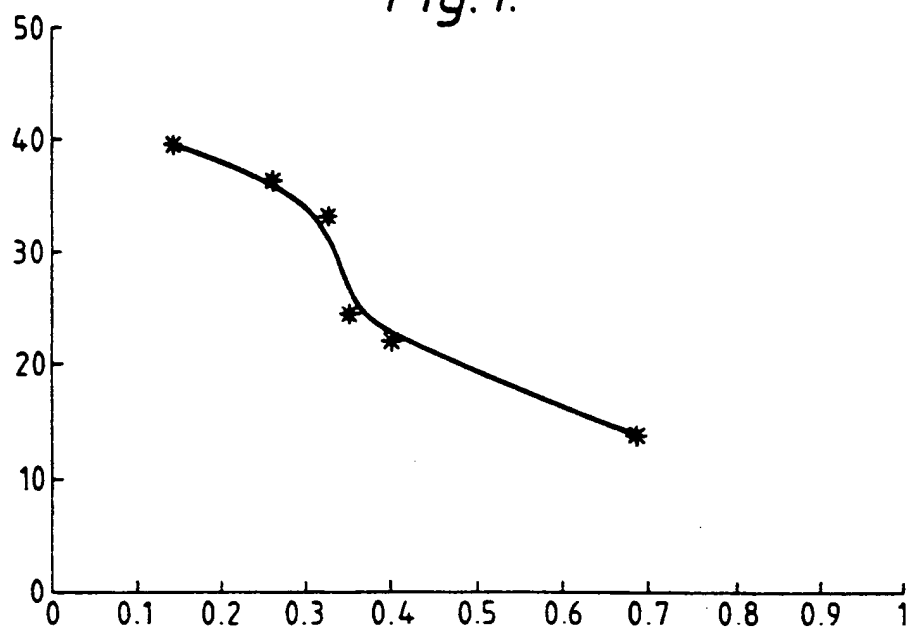
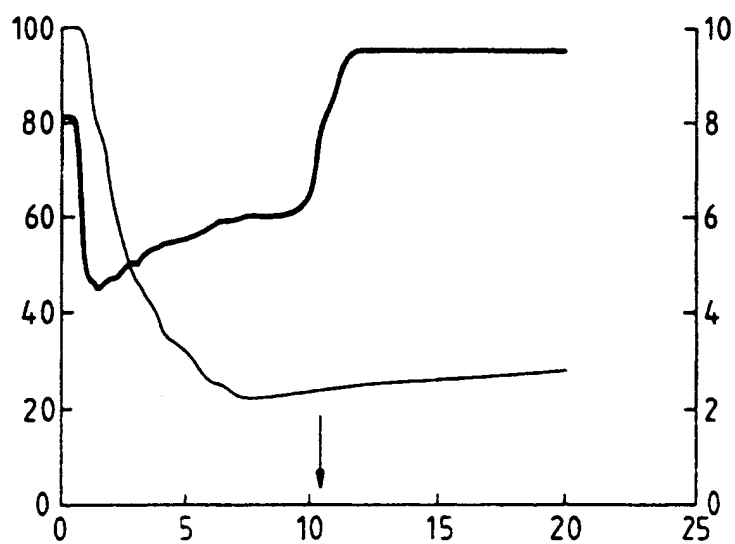
- 10 Experiments were carried out with ultrasonic radiation and deaeration similar to those described in Example 5. In this case, however, the ingredient mixtures described in Example 5 were pressed into two tablets, viz. a tablet A containing the citric acid/sodium bicarbonate/Na-dodecylbenzene
- 15 sulfonate mixture, and tablet B the remaining ingredients. Both tablets were added at the beginning of the wash; the results were similar to those obtained in Example 5, the degree of air saturation being reduced to less than 30% within 5 minutes, and the pH of the solution going from 6
- 20 to 9 between 7 and 12 minutes after the start of the wash.

The wash result on EMPA 101 was also at a similar level, i.e. practically the same as those mentioned in Table 2 for wash experiments with deaeration.

CLAIMS

1. Process for cleaning substrate in wash liquor with acoustic energy, characterised in that the wash liquor is degassed by using a chemical reaction.
5
2. Process according to claim 1, characterised in that during application of acoustic energy the wash liquor comprises less than 0.48 mmol/l of gas.
10
3. Process according to claims 1-2, characterised in that it involves adding gas to wash liquor whereafter a gas-to-non-gas converting system is activated.
- 15 4. Process according to claim 3, characterised in that the gas is carbondioxide.
5. Process according to claim 3, characterised in that the gas-to-non-gas converting system increases the pH of
20 the wash liquor.
6. Detergent composition suitable for use in acoustic energy washing processes comprising effervescent material and a release controlled gas-to-non-gas converting system.
25
7. Detergent composition according to claim 6, characterised in that the effervescent material comprises carbonate and acid material and the gas-to-non-gas converting system comprises a coated alkaline material.
30
8. Use of a detergent composition comprising effervescent material to achieve degassed wash liquor.
9. Use according to claim 8 characterised in that the
35 wash liquor comprises less than 0.48 mmol/l of gas.

1/1

Fig. 1.*Fig. 2.*

SUBSTITUTE SHEET (RULE 26)

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A	FR,E,60 160 (R. BAROT & G. FOUILLOUX) 23 September 1954 see the whole document ---	1,3,6,8
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INTERNATIONAL SEARCH REPORT

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